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IGNITION OF PROPELLANTS BY HOT GASES. PART I

15 OCTOBER 1953



U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

IGNITION OF PROPELLANTS BY HOT GASES. PART I

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ABSTRACT: The adiabatic compression of inert gases has been utilized as a means of studying propellant ignition. A novel feature of the compressor makes it possible to stop the compression stroke at very nearly the peak pressure and temperature and to hold the compressing piston at that position.

This machine has been used for fundamental studies of the rapid ignition of propellants by hot gases. Ignition can be obtained in a millisecond under appropriate conditions. The time delay before ignition seems heavily dependent on the rate at which energy is transferred to the surface. A theory relating the energy transfer rate to the frequency of collision of the gas molecules with the propellant surface, their average energy, and a proportionality factor is presented.

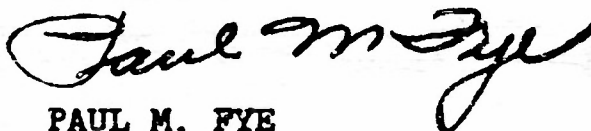
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By sudden, adiabatic compression of an inert gas temperatures and pressures are generated which are comparable to those in a gun during the ignition event. Experiments detailed in this progress report were designed to find how effective hot gases are for the ignition of propellants. This work is being continued under Task Assignment NOL-Re2d-02-1-53.

EDWARD L. WOODYARD
Captain, USN
Commander



PAUL M. FYE
By direction

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IGNITION OF PROPELLANTS BY HOT GASES. PART I

I. INTRODUCTION

A number of agents may impart energy to a propellant and thus bring about its ignition. Hot gases, hot particles, radiation, and chemically active radicals, ions, or molecules are the principal agents. Most primers contain several possible agents. For a clear understanding of ignition and intelligent design of new primers, more needs to be known about the relative importance of each of these agents.

We decided to try to obtain some fundamental knowledge on the action of hot gases in ignition. Others have worked in this field. Their work is subject to one or more of the three following disadvantages: (1) Other agents were not separated. (2) Their studies were at such low pressures or temperatures that ignition occurred on the order of seconds rather than the order of milliseconds found in use. (3) Some possibly important variables were not controlled or evaluated. We wanted to improve on past methods. A method was needed by which a hot, non-reactive gas could be rapidly applied to a propellant. It was further necessary that all important variables be measurable and adjustable.

Dr. E. C. Noonan and Mr. H. P. Feldman designed a machine for rapidly applying a hot non-reactive gas to a propellant, under controllable condition. This apparatus was constructed. The author added the instrumentation necessary for the measurement of the variables, and put it in operation. Mr. J. W. Enig and Mr. C. C. Ferriso assisted in this work.

This report furnishes a description of this apparatus and instrumentation and presents some early results from its use.

II. APPARATUS

A. Locked-Stroke Compressor

A diagram of this machine is shown in Fig. 1. It is used to rapidly compress a gas so that its pressure and temperature increase almost adiabatically. The compressing piston is arrested and locked at the end of the stroke. The pressure and temperature then fall due to cooling action, but this decrease is much slower than if the piston bounced back.

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At the beginning of a run, the locking piston, A, is pushed against the extended release pins, B. This prevents the gas in the reservoir, C, from moving either piston A or the compressing piston, D. The reservoir pressure will be from 150 to 500 psi, depending on the pressure in the compression cylinder, E. The compression cylinder pressure may vary from about 1/4 to 120 psi absolute.

When the release pins are retracted, both pistons are free to move forward. Both are accelerated and acquire momentum. As the pressure in the compression cylinder increases, the driving force due to the pressure differential decreases and eventually opposes the movement of the compressing piston. The momentums of the pistons plus the mechanical advantage of the locking piston are adequate to continue the compression when the front pressure is much higher than the reservoir pressure. The compression piston stops its forward movement when the links which connect it to the back of the reservoir chamber, F and F', are fully extended. The locking piston continues moving until the arresting projections, G & G', hit the stops, H & H'. This movement very slightly moves the compression piston backward, but the high pressure in the front of the piston no longer is able to push the piston back because the linkages are now elbowed toward the locking piston and the locking piston cannot move forward due to the stops.

The maximum point of the compression cylinder's movement can be varied by the adjustment at J. This adjustment also has a minor influence on the starting position. The cylinder can be made longer by adding spacers between the face-plate and cylinder end. The starting and final volumes, thus the compression ratio, can thereby be adjusted with ease.

The shock-absorber piston, K, is the most successful method which we have so far used to ameliorate the shock to the system and linkages which occurs when the projections hit the stops. This piston and rubber washer, L, is placed so that the end of the locking piston hits it at about a quarter inch from the stopping point. Part of the momentum is thus transmitted to the shock-absorber piston. The locking piston is thus decelerated over a longer period of time than would occur if the fixed stops were hit directly. This spares the system from considerable shock. The shock-absorber piston is caught in a padded tube.

B. Instrumentation

1. Pressure-Time Records - An analysis of the system indicated that a pressure-time record would be essential.

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The system used is practically identical to that described in NAVORD 2621 (1), so it will only be briefly described. An Aberdeen type C-AN gauge (strain wire wrapped on cylindrical ferrule) is used as the pressure transducer. Its output is put through a d.C. amplifier and recorded by means of an oscilloscope and a rotating-drum camera. The camera speed provides the time base. Appropriate signals are also injected for calibration purposes. The system used in the present work differs from that described in NAVORD 2621 principally by the following items: 1. The recording system is activated by a roller-contact micro-switch attached to the lever used to move the release pins. 2. The firing mechanism is not used. The gauge is mounted in the face-plate.

2. Time Record of Ignition - The propellant is mounted in front of a window and can be observed by an external photomultiplier tube. The point at which light first appears should give a high rate of change in the photomultiplier output. When the differentiated output of the photomultiplier is placed on the Z-input of the oscilloscope used for recording the pressure-time trace, the trace is intensified at that point. We thus have a pressure-time trace which is intensified at the first appearance of light.

The first intensification should always mark the ignition point. Fluctuations in intensity after ignition can also cause brightening or dimming, while the intensity is not saturating the photomultiplier. The end of ignition thus gives a dim portion followed by a short darkened portion due to RC oscillatory effects. This system has a very fast response and is principally limited by the clarity of the trace. On a good record, the point of ignition can be determined to within ± 0.15 millisecond.

The photomultiplier circuit is shown schematically in Fig. 2. It was intentionally kept simple and has performed excellently. It can undoubtedly be refined should the need arise, though additional recording circuits would probably be required to make refinements useful.

A small plastic window (Plexiglas) was placed in the face plate (see Fig. 3). It was designed by Mr. H. P. Feldman and a similar one was tested by Mr. T. K. Rice to 6000 psi. Its simplicity and excellent sealing should be useful to others. The hot combustion products cause surface blackening which can be easily removed.

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III. EXPERIMENTAL AND RESULTS

A. General

Early experiments were designed to explore the limitations and possibilities of the equipment and to acquire new ignition information on which more quantitative work could be based. Some of this work, though essential to progress, does not deserve detailed treatment. Details will thus be given quite selectively, with particular emphasis on the more quantitative ignition results.

B. Operation of Compressor

1. Modifications and Mechanical Sources of Error - It was quickly found that the apparatus would operate and that its main features were sound. Some of these improvements and some still existing troubles deserve mention.

Leakage of gas from or to the compression cylinder is considered negligible, because none is detectable within the precision of our best measurements ($\pm 0.6\%$). This was tested several times after a full cycle of compression and decompression when the piston bounced due to inadequate driving pressure, and also by static methods. This good sealing was obtained by replacing the original 4 automotive type piston rings by a single "O" ring and by holding the piston fit to close tolerances (order of a few ten-thousandths of an inch).

The original locking piston was designed with close tolerances in fit. This gave serious friction troubles due to galling from small fragments sheared from the release pins. Changes in the shape and hardness of the pins was helpful, but this problem was still troublesome until the locking piston was greatly reduced in diameter, except near the "O" ring seals.

Originally, the locking piston cushioned its stopping by compressing air between its end and a movable closure. This was unsatisfactory because adequate cushioning pressures prevented the locking action. The present shock-absorber system combined with numerous strengthening modifications throughout the system makes it possible to make a reasonable number of runs before repairs are necessary. In addition to wear, shocks also make the pressure-time trace noisy. If the driving pressure is just right, there is very little shock. Unfortunately, this adjustment is still partially guesswork, due to variations in friction, starting pressures, compression ratios, and gases.

The slight backward movement of the piston before it is locked causes the pressure-time trace to show a rather rapid

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drop for several milliseconds after the peak. This hump in the trace (see Fig. 4) becomes larger as the compression ratio is increased, because the per cent change in volume is larger. This hump has some important effects which will be discussed later. The hump can probably be decreased some by advancing the stopping point.

In addition to the main volume in the compression chamber, there are small volumes to which the gas has access. These are principally due to "O" ring clearances, piston to cylinder wall clearances, and volumes of connecting tubes and valves. This total volume was calculated to be equivalent to a piston movement of .029", but their area to volume ratios are quite large. This means that cooling occurs very rapidly in such volumes and thus effectively magnifies their size by a factor approaching the temperature in the chamber divided by the wall temperature. This effect becomes more serious as the compression ratio is increased because the effective volume due to the small volumes increases and the volume in the main chamber decreases. The behavior is further complicated by flow rates which are involved in the movement of a gas through small passages. On chamber cooling there will also be an effect due to the extra volumes supplying molecules to the main volume. It is believed that these extra volumes can be reduced by decreasing the clearances for the piston "O" ring and moving it to a position nearer the front of the piston.

2. Useful Operating Ranges - Rapid compression can be obtained over a large range of compression ratios. The final 80% of the pressure rise usually takes place in 2.5 - 3.5 milliseconds, but can be varied between 2.0 to 5.0 milliseconds by appropriate driving pressure adjustments. The useful range of compression ratios is from 4 to 30.

The maximum temperatures obtainable vary with the gas. Temperatures of 2000°K have been obtained with Helium ($\gamma = 1.67$) and higher temperatures should be easily obtainable. For nitrogen ($\gamma = 1.40$) the upper temperature obtainable is about 1200°K, unless the starting temperature is higher than 300°K.

The maximum usable pressure is determined by the strength of the apparatus and is roughly 3000 psi. It is harder to obtain high pressures if compression ratios or gammas are low, as the pressure in both the compression chamber and driving reservoir must be high. Such runs cause the equipment to wear rapidly. High pressure data are thus harder to obtain

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for nitrogen than for helium or argon and even with monatomic gases are hard to obtain at low temperatures.

3. Variables and Their Control - We feel that we are definitely dealing with ignition by hot gases. Neither helium, argon, nor nitrogen should yield ions or free radicals in any significant quantity under the conditions so far employed, nor should they react chemically. No hot solids are present. The hot gases are the only possible source of radiation and are all low in radiation. Except at high temperatures where possibly a small amount of energy may be transferred by radiation, the initial heating of the propellant to its decomposition point must be due to heat transfer processes which involve collision with the gas molecules.

The time of ignition can be estimated to ± 1.5 millisecond.

The amount of energy per unit volume of gas depends on the pressure, temperature, heat capacity of the gas, and the gas laws. For the particular gases used, the heat capacities are known fairly precisely.

The precision of pressure measurements is roughly $\pm 1\%$ and the accuracy will vary from about 1 to 3%, being worst at low pressures for dynamic measurements.

Temperature measurements are based on pressure. Ideally, for an adiabatic compression --

$$P=P_1(V_1/V)^{\gamma}, \quad T=T_1(V_1/V)^{\gamma-1} \quad \text{and} \quad T=T_1(P/P_1)^{\frac{\gamma-1}{\gamma}}, \quad \text{where}$$

P=pressure, T=temperature in $^{\circ}\text{K}$, V=volume, γ =ratio of molar heat capacities (C_p/C_v), and i=initial. After the piston locks and the volume becomes fixed -- $T=T_1 P/P_1$, where L signifies conditions at locking time.

It is important to note that pressure and temperature can be independently adjusted, the temperature during compression being dependent only on the compression ratio and initial temperature. The peak temperature is thus fixed when the compression ratio is fixed, if the initial temperature is fixed. The initial pressure can be varied so as to vary the peak pressure.

Errors in temperature due to errors in pressure are smaller than the pressure error during compression and equal to the pressure error after locking.

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Changes in gamma for nitrogen (which should be far worse than helium or argon in this respect) should not change temperatures by more than a few per cent even at temperatures of 1200°K and pressures of 100 atm. This estimate was based on recent data (2,3).

Errors in temperature due to cooling are difficult to calculate, as the amount of error depends on the temperature distribution. If we assume, as Ffrien does (4), that such cooling influences the central chamber gases only by effectively allowing these gases to expand, then the error introduced by our pressure-based calculations will still be small even at high compression ratios. Cooling which occurs before locking can cause errors in temperatures calculated after locking. Cooled gases in the extra volumes (see II-B-1) and any other cool layers that may be present act as pressure reservoirs and distort the cooling curve. Cooling definitely should increase with an increase in the compression ratio, due to higher temperature gradients between the gas and the wall, an increase in the ratio of small extra volumes to the main volume, and an increase in the ratio of surface to volume for the main volume. Our best calculations and measurements indicate that temperature errors from cooling are no more than a few per cent over a large range of conditions, but may possibly be much larger at high compression ratios.

C. Ignition Experiments and Results

1. Propellants and Gases Used - So far, only N-4, JPN, JPH, and SPDN propellants have been used. A number of early, rough tests were performed with JPN and JPH, but only several tests were made with SPDN. It was then decided that it would be better to explore one propellant somewhat precisely before acquiring data on a number of propellants. Most of the tests have been made with N-4 propellants. Though rather new, N-4 was chosen because it does have large scale use, contains high percentages of nitrocellulose and nitroglycerin (both being common to many propellants), was immediately available in pieces which were large enough to try a variety of shapes, and its physical properties were such that it could be easily cut and shaped.

Nitrogen, helium, and argon have been used as working gases. (The same gas is always used for ignition and operation.) Helium and argon have the same gammas and molar heat capacities, but the molecular weight of argon is ten times that of helium. Nitrogen is the only diatomic gas which is essentially inert. It, of course, has a different gamma and molar heat capacity. Other gases, CO₂ for instance, may be included in the future.

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2. Preparation of Propellant Samples and Its Importance - N-4 samples were usually prepared in the following way. 16 to 20 discs were cut from microtomed sheets of 120 microns thickness. These were stacked on a wire at spacings of .016 to .025 inches and mounted as is schematically shown in Fig. 3. Two disc diameters, 5/32 and 7/32 inch, have been used. In the ranges of numbers, spacings, and diameters given, results are reasonably reproducible.

The above choice was somewhat fortunate according to recent tests on the effects of the propellant's geometry and dimensions. Ignition lags (see III-C-4) are shortest at a spacing within the above used range, but decrease sharply with much greater or smaller spacings. Ignition lags (for the critical spacing range) decrease rapidly at first as more than one disc is used, but become nearly asymptotic by the time 5 discs are used, changing very little with larger numbers. Ignition lags for larger diameter discs are shorter when only a few discs are used, but differences rapidly disappear as the number of discs increase. These tests are still continuing and will be detailed in a later report.

Other types of samples have been used, but the bulk of the data in this report is on the type detailed above. Other types will not be discussed here but will be mentioned where results using such samples are included.

3. Ignitability Comparisons between Propellants - All four types of propellants (N-4, JPH, JPN, and SPDN) were successfully ignited with our apparatus. JPN and JPH were widely used in our early work and were tried in a variety of test sample shapes, varying from 80 microns thick sheets and strips to rough hunks. SPDN was tested in the form of a disc sawed from a perforated cylindrical grain. These differences in shapes make comparisons difficult. JPN and JPH seemed qualitatively to be much easier to ignite than N-4, but no completely comparable tests have been made. No comparisons are possible with the SPDN because of its different shape.

4. Rapidity of Ignition - Early tests were designed to see if ignition could be obtained with the apparatus. It was quickly established that ignition could be obtained. Further work showed that it could be obtained during the compression stroke or at a much later time. In other words, ignition of a propellant can occur in from one to greater than 400 milliseconds after being exposed to a hot gas, the time depending on the conditions. This dependence will be discussed under other headings.

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"Ignition lag" is herein employed to signify the time between the peak of the compression stroke and the time at which ignition occurs. It is thus a measure of the rapidity of ignition. It will be negative when ignition occurs before the peak. For some purposes it is desirable to include corrections for the compression time. It has been found that ignition lags may be increased by increasing the compression speed (thus decreasing the heating time during compression). Two tests (using N-4 propellant and helium gas) for which the final 80% of the pressure rise occurred in 3.3 milliseconds gave an average ignition lag of 5.6 milliseconds compared with 3.4 milliseconds for two tests which were identical except for longer compression times of 4.5 milliseconds for the final 80% of the pressure rise.

5. The Influence of Pressure and Temperature on Ignition - An early investigation of these factors was done with JPH propellant. In each of these runs a single thin sheet of propellant was used ($3/4$ " x $9/8$ " x 80 microns). Nitrogen was used as the working gas. Though rough, these results were interesting. They showed that for a given peak temperature there was a fairly definite limit to which the peak pressure could be lowered if ignition were to be obtained. This limit decreased for one variable as the other variable increased. The results are plotted in Fig. 5. At that time, a very rough method of estimating ignition by pressure rises was being used. This method and later precise, photomultiplier estimations for N-4 indicated that ignitions resulting from conditions near those just sufficient to cause ignition were quite slow.

As we were particularly interested in rapid ignition, most of our later work employed higher pressures and temperatures and was based on ignition lags (see 4, above) rather than the occurrence or non-occurrence of ignition. We have in general characterized our pressure-time curves by their peak pressures and temperatures.

It was quickly shown that ignition lags decreased with an increase in either the peak pressure or temperature. Some of these tests and results are shown in Tables 1 and 2. Although there is clearly some scatter in the data, the above-mentioned trends are obvious. Some of the scatter is undoubtedly due to variations in compression speeds. Comparisons between gases may also have been affected by compression speeds (see III-C-4). Nitrogen tests seem generally to have had faster compressions than helium or argon. This was due to the effect of nitrogen's lower gamma on the experimental conditions necessary for obtaining a given pressure.

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A different approach was tried in the hope that the fundamental basis of the temperature and pressure effects might be brought out. A series of runs were made to determine the minimum conditions necessary to bring about ignition in one millisecond after the peak. In Fig. 6 is shown a schematic representation of how the ignition lag varies with pressure. All the curves shown are for one compression ratio and thus one peak temperature, but different pressure-time curves are obtained by varying the initial pressure. From such a set of curves we select the one for which ignition occurs at one millisecond after the peak. We then obtain a new set of curves by changing the compression ratio and thus the peak temperature. We again select the curve for which ignition occurred one millisecond after the peak. We continue this until we have a number of one-millisecond-ignition-lag curves. We then plot the peak pressures and temperatures for these curves, as is actually done in Fig. 7 for ignition of N-4 by helium.

A fairly regular behavior is shown until about 1450°K, where there seems to be a sharp drop in the pressure required for ignition. As temperature measurements are more uncertain in this region, further work will be required to show that such a drop is real. Present calculations indicate that the errors should make the apparent temperature higher than the actual temperature. If this is correct, the drop must be real and may have considerable significance.

It should be noted that conditions below the curve should give slower ignition and conditions above the curve should give faster ignition than for conditions along the curve.

Several points were also obtained for nitrogen on such a curve. These fell far above the points on the helium curve. In other words, nitrogen requires more stringent conditions than does helium for equal ignition lags. Argon requirements are also higher than for helium.

IV. DISCUSSION OF SOME FACTORS IN IGNITION

If the total amount of energy delivered by the gas up to ignition were the controlling factor, then we would not

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expect ignition to occur after the gas cooled below the decomposition temperature of the propellant. Yet such does occur. It can also be shown that in ignitions with long ignition lags the propellant receives more energy than when ignition lags are short.

Others have suggested that the amount of energy in the gas that was available for transfer might be the controlling factor. If this were true, under equal conditions of pressure and temperature nitrogen should give more rapid ignition than helium, as nitrogen has a higher molar heat capacity. Exactly the reverse is true.

A propellant must decompose at some point before it will ignite. Ordinarily, a small increase above the decomposition temperature will cause a large increase in the decomposition rate. Once decomposition begins, a second source of energy is available from the decomposition or further reaction steps and ignition may possibly occur without further energy being supplied from the first source. The additional time spent before ignition would still be heavily influenced by the initial amount of decomposition caused by the first source.

From this it is apparent that factors which control the surface temperature may be extremely important. The properties of the propellant are, of course, important. The most important factors external of the propellant properties are the rate at which energy is transferred to it, or heat flux, and the duration of such transfer. Furthermore, if we have a given amount of energy to apply to a surface, the higher the rate of application the higher will be the surface temperature, even though the time of application must be proportionally shorter. In other words, a small amount of energy applied at a very high flux may cause a higher surface temperature than a much greater amount of energy applied at a low flux. From the above it can be seen that a short interval of exposure to a high heat flux may easily control ignition.

V. DEVELOPMENT AND APPLICATION OF A HEAT TRANSFER THEORY

1. Introduction - The data already presented shows that there is a qualitative relationship between peak conditions

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and ignition lags. Application of the above conclusion, that short intervals of high heat flux may control ignition, gives a physical basis for this correlation. It would be expected that the maximum heat flux would not be far removed from the peak of compression. It is thus not unreasonable to expect that the highest surface temperature directly resulting from heating by the inert gas would occur very close to the peak. This temperature would heavily influence the amount of initial decomposition and thus the time required for further reaction to lead to ignition.

The minimum conditions curve was obtained with the idea of using the data for heat flux calculations. Runs which gave equal ignition lags should have similar surface temperature versus time histories. The conditions necessary for a fixed ignition time would be roughly-equal flux-time histories. If the data along the minimum conditions curve were fitted into an equation for flux calculations, a constant should be obtained.

The joker to this was that no suitable equation could be found for the pressures, temperatures, and transient conditions involved. Recently, the author did find an article by Pfriem (4) which developed such an equation for the minimum flux to be expected for a metal surface, but no experimental proof was given. We applied this equation to one of our pressure-time curves and found that it predicted a much smaller flux than could have caused ignition by the time that ignition had actually occurred. Furthermore, the calculations were very laborious. He does clearly present one important factor. Heat flux should be greatly increased during a compression over that for fixed volume conditions. The reverse holds true for a decompression. This lends further support to the belief that heating occurring during the compression would be particularly important. The slight decompression which occurs before locking should serve to sharply decrease the flux after the peak.

In the absence of usable equations the author tried some simple treatments of data, including some rough calculations of heat flux based on collision frequencies and energies. These results were promising and were further developed. Heat transfer work at very low pressures (generally listed under "accommodation coefficients") has been quite useful in many respects. High pressure work using collision energies and frequencies has been largely neglected, because results were a number of magnitudes too high when based on total gas temperatures. Accommodation coefficient investigations can be readily surveyed by using the well-referenced works of

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Loeb (5), Partington (6), and Schäfer (7). Thomas and Brown's work (8) on the influence of temperature differences between the solid and gas on the accommodation coefficient is a valuable recent reference.

2. Development of a Heat Transfer Equation - The product of the energies and collision frequencies of the molecules hitting a surface can be considered as an upper limit for heat flux. This upper limit can then be reduced by a factor. Even if this reduction factor is very large, the equation will be valuable if this factor is easy to calculate or experimentally obtain, or is roughly constant. If even relative values for various gases can be obtained, we have a qualitatively useful tool.

By using calculations similar to Knudsen's (9) we obtain for the energy-frequency product --

$$\frac{dQ}{Adt} = \frac{2.99PT^{1/2}(\gamma+1)}{M^{1/2}(\gamma-1)} \text{ in cal./sec.cm.}^2, \text{ where } Q=\text{energy,}$$

A=area, t=time, γ =ratio of molar heat capacities (C_p/C_v), and for the constant used P=pressure in psi, T=temperature of gas in degrees K, and M=molecular weight of the gas in grams. It is interesting to note that $(\gamma+1)/(\gamma-1)$ is equal to the number of active degrees of freedom of the molecule plus one. The extra one is due to the fact that faster molecules collide more frequently with a surface so that the average translational energy of the colliding molecules is $kT/2$ greater than the average translational energy of the molecules in the gas.

The reduction factor may be represented as the product of a number of dimensionless weight factors, each having some physical significance. The first of these is based on the fact that on the average the temperature of the gas molecules after collision will not be less than the temperature of molecules colliding with the surface from a gas at the surface temperature. This factor will at present be set at $(T-T_s)/T$, where T=temperature of gas and T_s =Temperature of surface. The remaining weight factors will be represented by $G_2, G_3, \dots G_n$. We then have --

$$\frac{dQ}{Adt} = \frac{2.99PT^{1/2}(\gamma+1)(T-T_s)G_2G_3\dots G_n}{M^{1/2}(\gamma-1)T},$$

for which the above units and symbol meanings hold.

3. Application of Heat Transfer Equation - The results of applying this equation to the minimum conditions curve (Fig. 7) and two points for a nitrogen curve are shown in Table 3. The heat flux values are fairly constant whether the G_1 factor is evaluated or not and the nitrogen values are not far from the helium values. The equation thus gives the predicted results over a wide range of pressures and temperatures and gives moderate agreement between the two gases even though there are large differences in pressures and molecular weights. T_s was assumed to be 500°K in the evaluation of G_1 . The basis of this was that one would expect that the surface temperature would be at or near its decomposition temperature when exposed to the peak flux.

We then tried applying this flux equation to a large mass of data. In Figs. 8 and 9 are shown log-log plots of functions of the peak flux versus delay time for helium, argon, and nitrogen on N-4 propellant. Fig. 8 evaluates G_1 as above and this is effective for making the lines parallel. In Fig. 9 G_1 is not evaluated and this effectively gives the same slopes and values that would be obtained if the surface temperature were assumed to be zero or to have no effect. If a value of 300°K had been assumed for T_s , then the slopes and values would have been between those of Figs. 8 and 9.

From Fig. 8 three important observations can be made. There does seem to be a regular relationship between the fluxes at the peaks and ignition lags. The curves have roughly the same slopes for all three gases. The values of fluxes for a given ignition lag divided by the product of the unevaluated G factors vary somewhat with the gas.

The ignition lags seem quite sensitive to a change in flux. This is in line with the fact that even a small change in surface temperature should give a large change in the decomposition rate of the surface.

The fact that the lines for the three gases have similar slopes together with the assumptions that equal ignition lags correspond to equal fluxes suggests that the ratio of $G_2 \times G_3 \times \dots \times G_n$ for one gas to the same product for another gas is constant over a wide range of pressures and temperatures. From this it follows that for a given gas this product may be constant over a wide range of pressures and temperatures

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or else that the products for the three gases may have a similar dependence on flux.

The variations among the three gases in the values for the plotted function $(\text{flux}/G_2G_3\text{---}G_n)$ at a given ignition lag suggests that one or more of their G factors should be more fully evaluated. The flux requirements should not change with the gas. The equation for each G factor must be the same from gas to gas. The G factors involved in this variation must thus depend on some property which changes from gas to gas if the numerical values of the G factors are to change from gas to gas. The most logical basis for attack seems to be the effect of molecular weights on the accommodation coefficient. In general the accommodation coefficient of a gas will increase with its molecular weight. The G factor assigned to this would thus decrease helium values the most and argon values the least.

The calculation of such molecular weight factors has been attacked by a number of investigators, but still appears to be in an unsatisfactory state. The rough magnitudes would seem to be about right to bring helium down to the argon level. With nitrogen it is also possible that lower accommodation coefficients operate on non-translational energy exchanges and compression speeds may have had some effect (see III-C-4 & 5). The author is trying to use available data to predict these factors, but prefers at present to leave them for future application.

4. Further Discussion of G Factors - The G factors may be usefully divided into two types, those operating on the collision and exchange processes and those operating on pre-surface-collision processes (due to temperature gradients, concentration gradients, etc.) The latter type shows some promise of being roughly constant. The former can probably be partially determined by experimental methods, possibly by low pressure work of the accommodation coefficient type. In many cases the value of existing data is impaired by the almost universal use of the solid as the heat donor and the use of metals as the solids.

VI. SUMMARY OF RESULTS AND CONCLUSIONS

1. Both Pressure and Temperature are important in ignition by hot gases. An increase in either increases the rapidity of ignition.

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2. A high rate-of-energy-transfer of only short duration may be very important in ignition.

3. An equation based on the energies and frequencies of collision of gases with surfaces shows considerable promise for predicting energy-transfer-rates under high temperatures and pressures and under transient conditions, particularly for comparative purposes.

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9. See 5 above -- pages 314-317.

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TABLE 1
THE INFLUENCE OF PRESSURE ON IGNITION

| Test # | Gas and Propellant | Peak Temperature °K | Peak Pressure psi | Ignition Lag Milliseconds |
|--------|-----------------------|---------------------------|-------------------------|---------------------------------|
| 116 | Helium and N-4 | 907 | 391 | No ignition |
| 117 | | 907 | 957 | 86 |
| 152 | | 900 | 1011 | 50 |
| 118 | | 942 | 1060 | 17.6 |
| 129 | | 939 | 1665 | 0.6 |
| 112 | | 1162 | 1060 | 8.7 |
| 113 | | 1167 | 1342 | 0.5 |
| 108 | | 1252 | 1072 | 1.0 |
| 110 | | 1260 | 1236 | 0.9 |
| 111 | | 1255 | 1296 | 0.0 |
| 95 | | 1393 | 1079 | 3.5 |
| 93 | | 1379 | 1144 | 0.0 |
| 80 | | 876 | 1025 | 354.0 |
| 81 | | 880 | 1262 | 46.9 |
| 129 | | 882 | 2264 | 1.5 |
| 130 | | 887 | 2473 | 1.2 |
| 153 | | 860 | 2937 | 0.8 |
| 126 | | 905 | 2098 | 2.2 |
| 128 | | 915 | 2432 | 0.8 |
| 175 | | 930 | 1018 | 27.6 |
| 179 | | 918 | 1897 | 5.5 |
| 169 | | 1130 | 1651 | 5.0 |
| 172 | | 1110 | 1966 | 0.0 |
| 173 | | 1140 | 1953 | 1.9 |
| 165 | | 1295 | 1372 | 10.6 |
| 166 | | 1282 | 1721 | 4.3 |
| 167 | | 1250 | 1965 | 0.5 |

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TABLE 2
THE INFLUENCE OF TEMPERATURE ON IGNITION

| Test # | Gas and Propellant | Peak Temperature °K | Peak Pressure psi | Ignition Lag Milliseconds |
|--------|--------------------|---------------------|-------------------|---------------------------|
| 117 | Helium and N-4 | 907 | 957 | 86.4 |
| 124 | | 1665 | 939 | 0.6 |
| 152 | | 900 | 1011 | 49.6 |
| 105 | | 1350 | 995 | 3.8 |
| 122 | | 1612 | 1002 | 0.0 |
| 149 | | 875 | 1092 | 45.8 |
| 135 | | 1927 | 1077 | 0.0 |
| 81 | Nitrogen and N-4 | 880 | 1262 | 47 |
| 134 | | 1075 | 1246 | 14.8 |
| 165 | Argon and N-4 | 1295 | 1372 | 10.6 |
| 184 | | 1842 | 1383 | 4.3 |

TABLE 3
CALCULATED HEAT FLUX ALONG CURVE IN FIG. 4

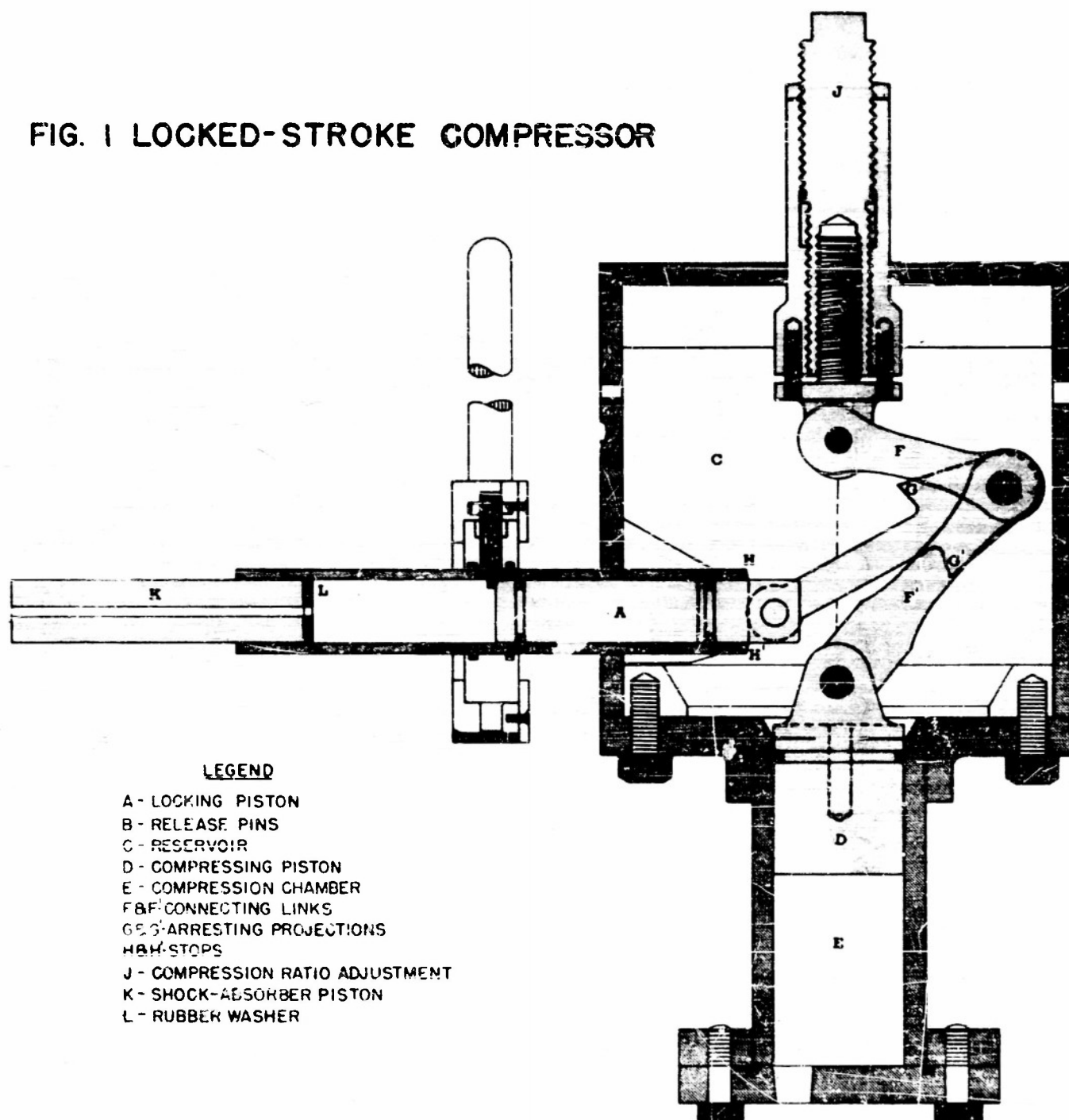
| Gas and Propellant | Temp. °K | Pressure psi | $dQ/AdtG_1G_2--G_n$ cal/cm. ² sec | $dQ/AdtG_1G_2--G_n$ cal/cm. ² sec |
|--------------------------|----------|--------------|---|---|
| Helium and N-4 | 1000 | 1420 | 2.69×10^5 | 1.34×10^5 |
| | 1100 | 1380 | 2.74 | 1.50 |
| | 1200 | 1330 | 2.75 | 1.61 |
| | 1300 | 1270 | 2.74 | 1.69 |
| | 1400 | 1140 | 2.55 | 1.64 |
| | *1465 | 954 | 2.16 | 1.42 |
| N ₂ Δ and N-4 | 860 | 2937 | 2.92 | 1.24 |
| | 933 | 2629 | 2.72 | 1.26 |

* High temperature effect present

Δ Not in Fig. 4, but for same ignition lag of one millisecond vicinity.

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FIG. 1 LOCKED-STROKE COMPRESSOR



LEGEND

- A - LOCKING PISTON
- B - RELEASE PINS
- C - RESERVOIR
- D - COMPRESSING PISTON
- E - COMPRESSION CHAMBER
- F&F' - CONNECTING LINKS
- G&G' - ARRESTING PROJECTIONS
- H&H' - STOPS
- J - COMPRESSION RATIO ADJUSTMENT
- K - SHOCK-ABSORBER PISTON
- L - RUBBER WASHER

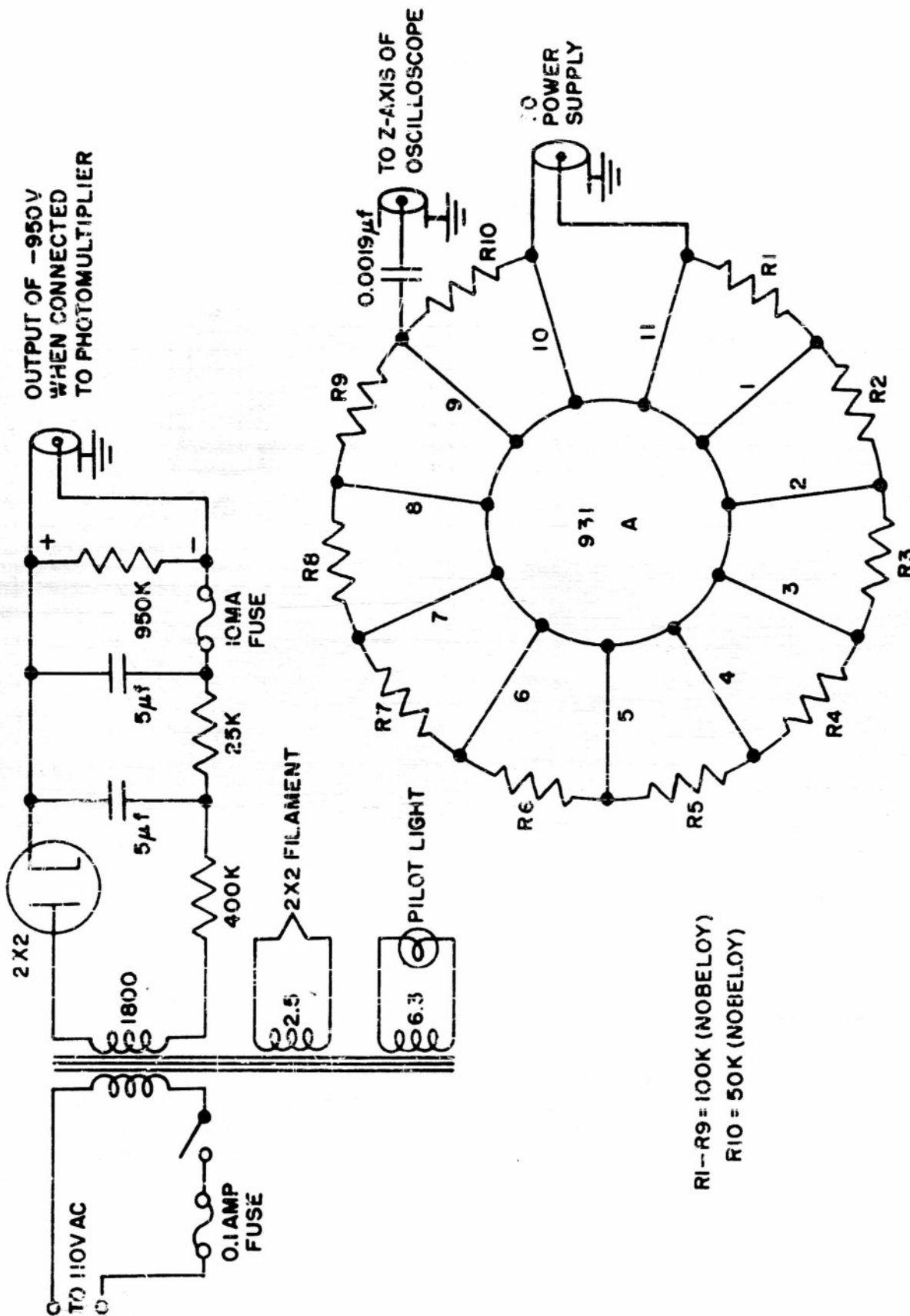


FIG. 2 PHOTOMULTIPLIER CIRCUIT

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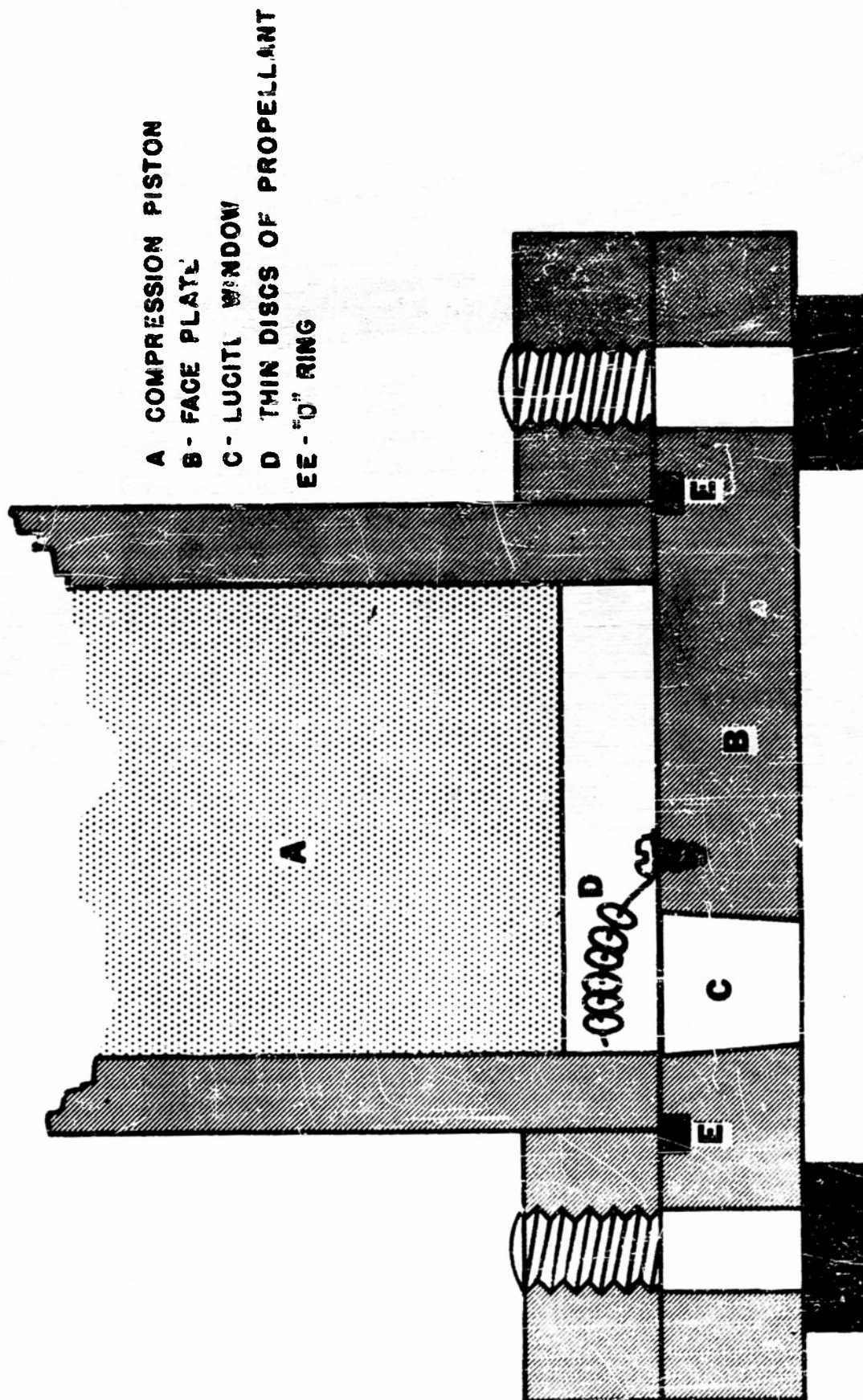


FIG. 3 COMPRESSION CHAMBER AND PROPELLANT MOUNTING

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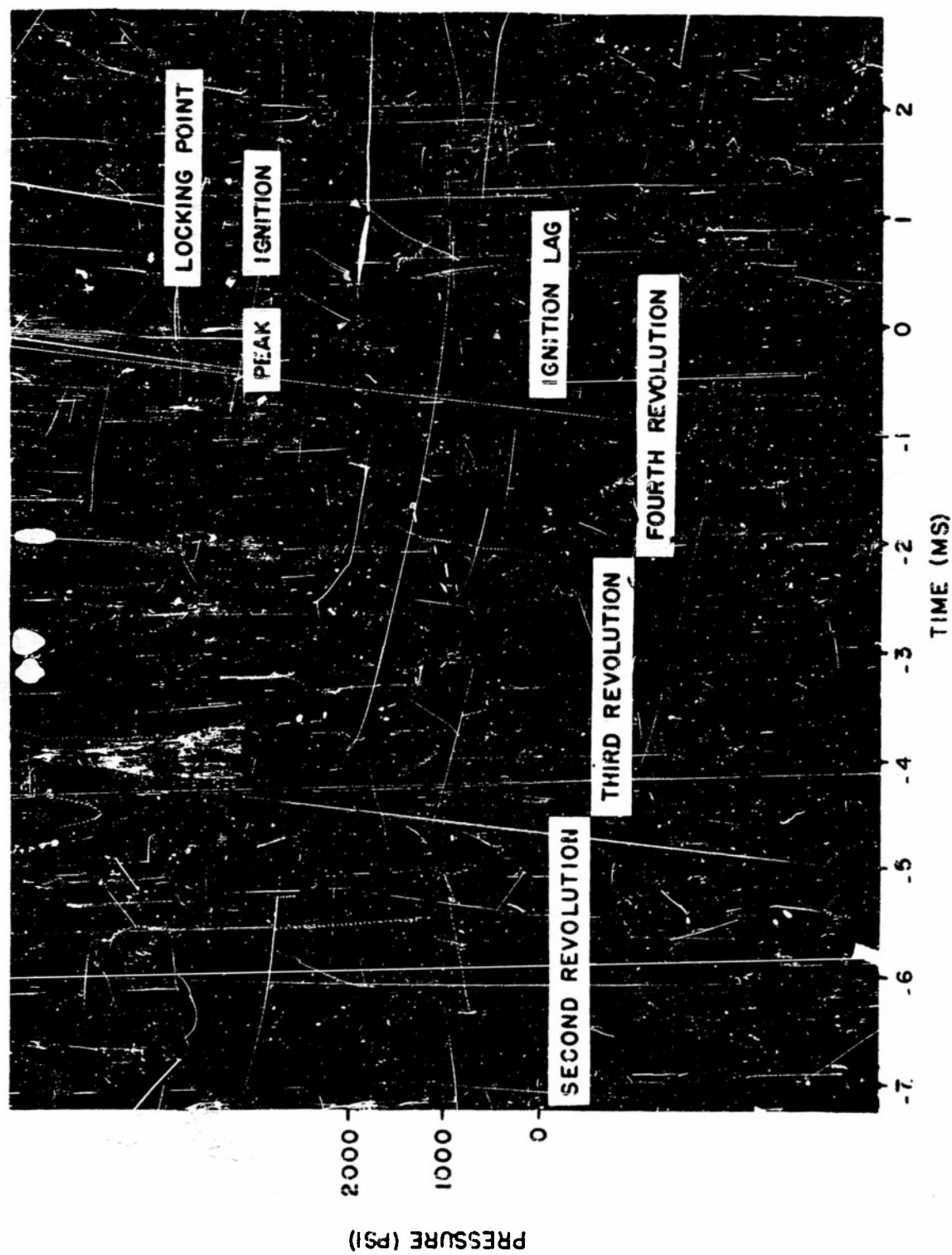


FIG. 4 ENLARGED SECTION OF PHOTOGRAPHIC PRESSURE-TIME TRACE

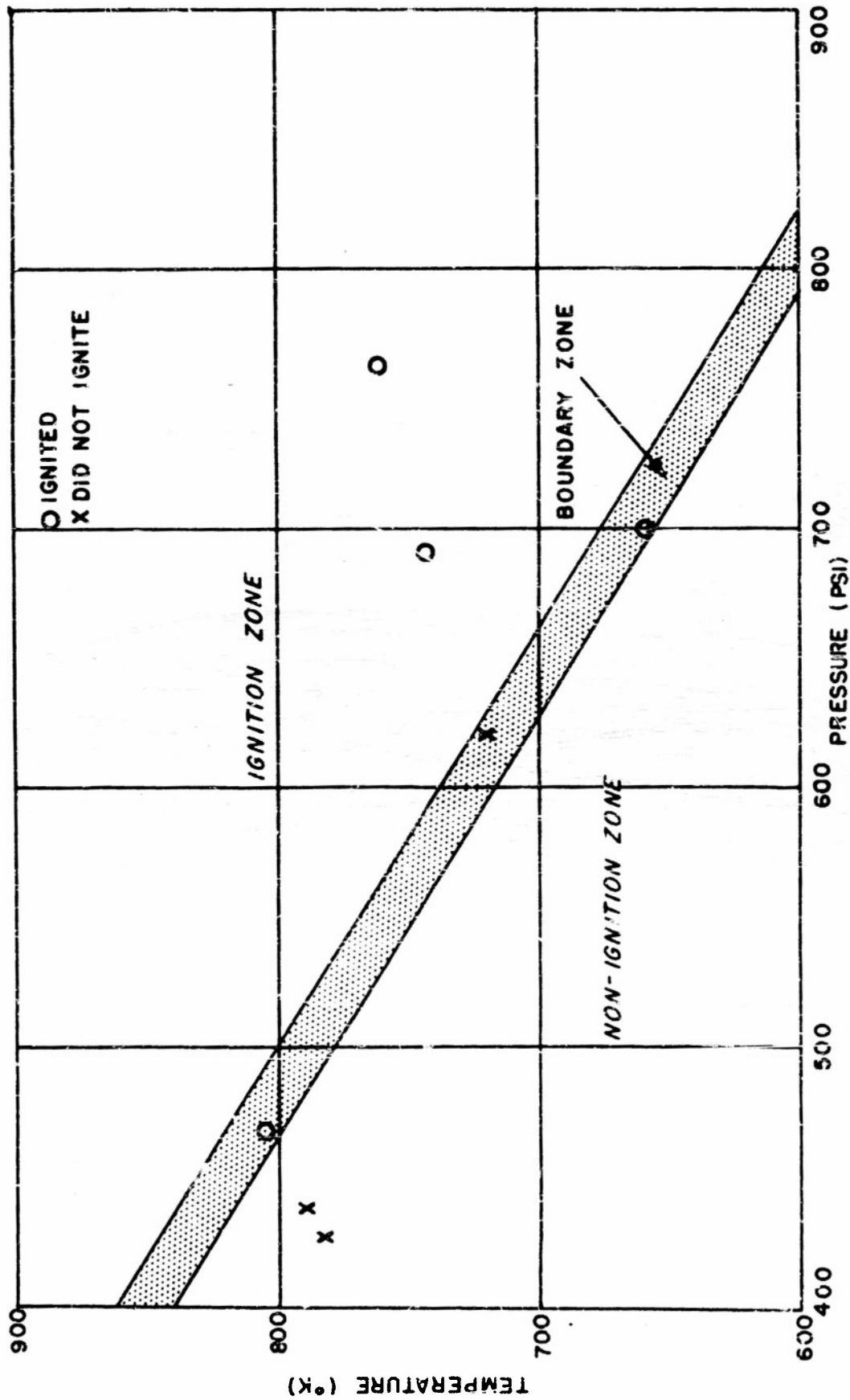


FIG.5 VARIATION OF IGNITION PROBABILITY FOR JPH WITH PRESSURE AND TEMPERATURE OF NITROGEN

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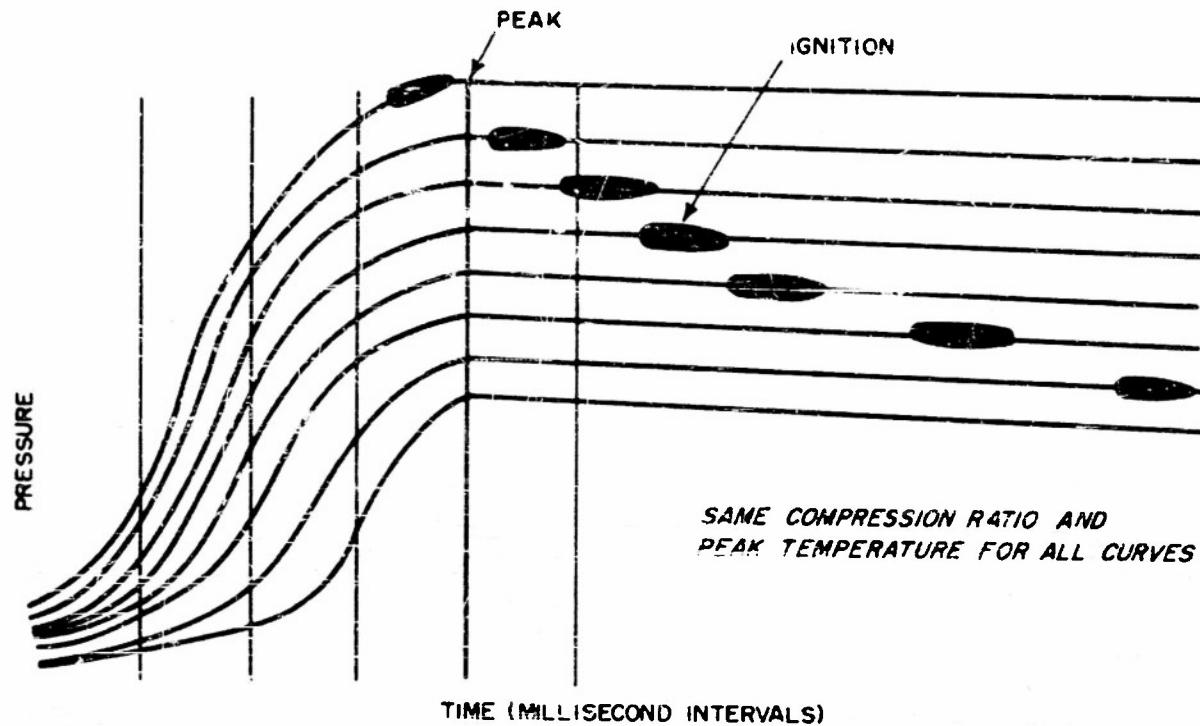


FIG. 6 CHANGE OF IGNITION LAG WITH PRESSURE

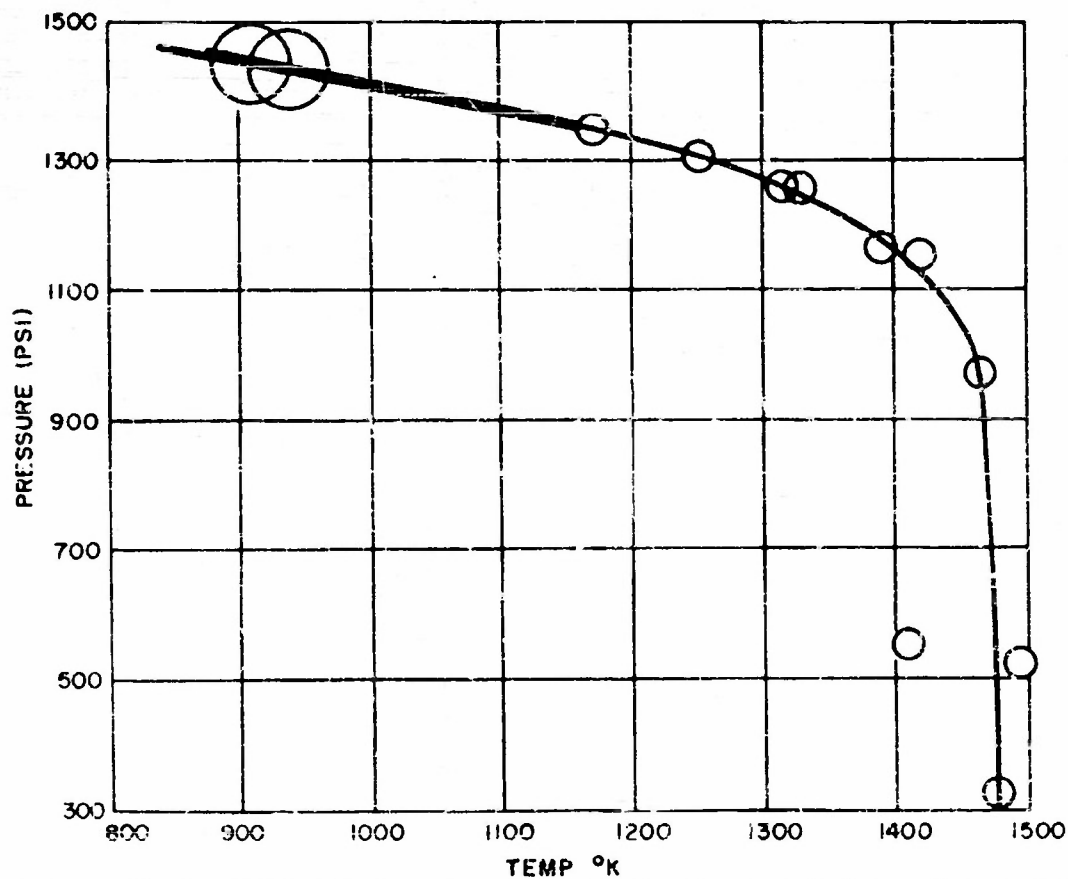


FIG. 7 MINIMUM CONDITIONS REQUIRED TO GIVE

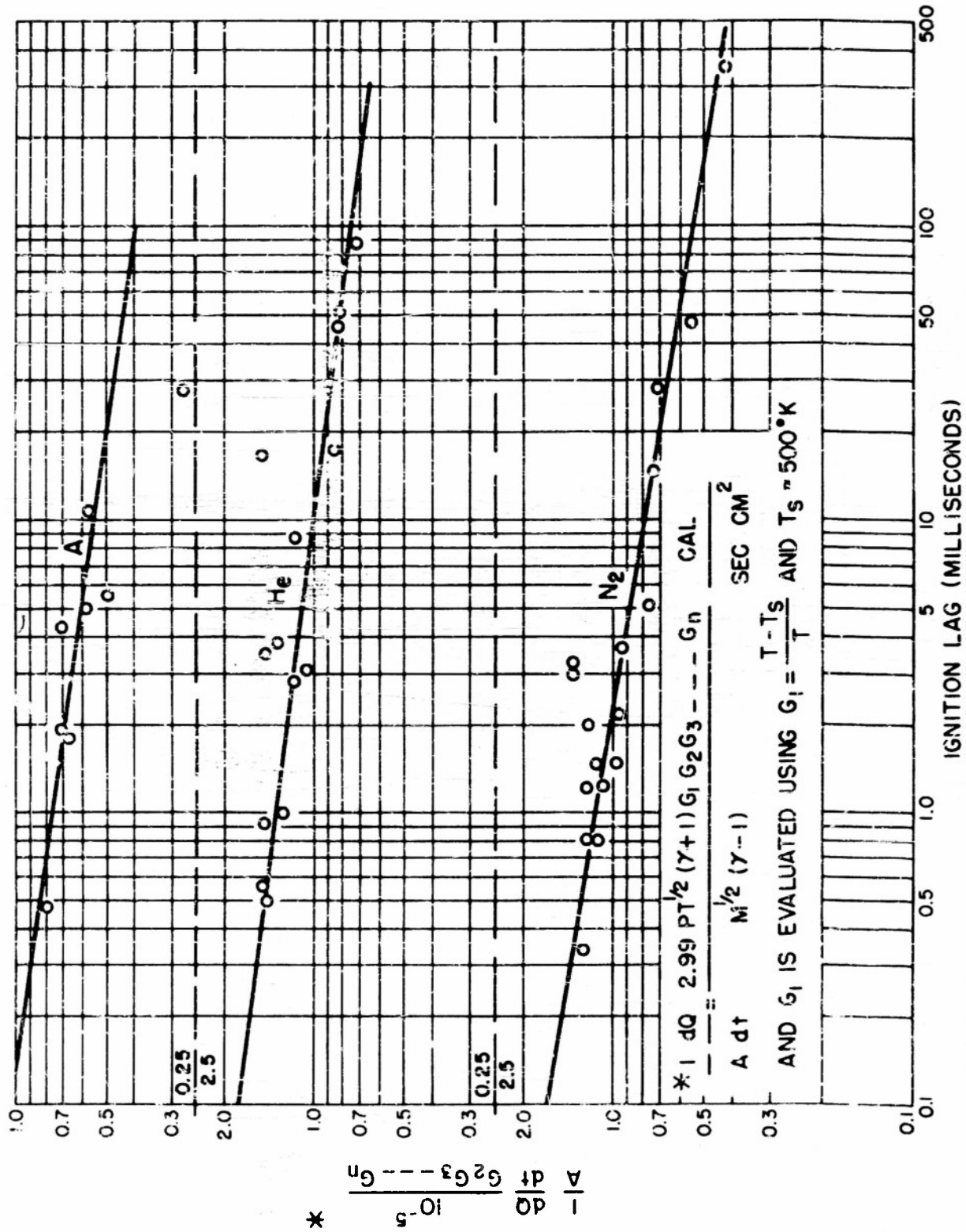


FIG. 8 FUNCTION OF HEAT FLUX VS IGNITION LAG
(CORRECTED FOR SURFACE TEMPERATURE)

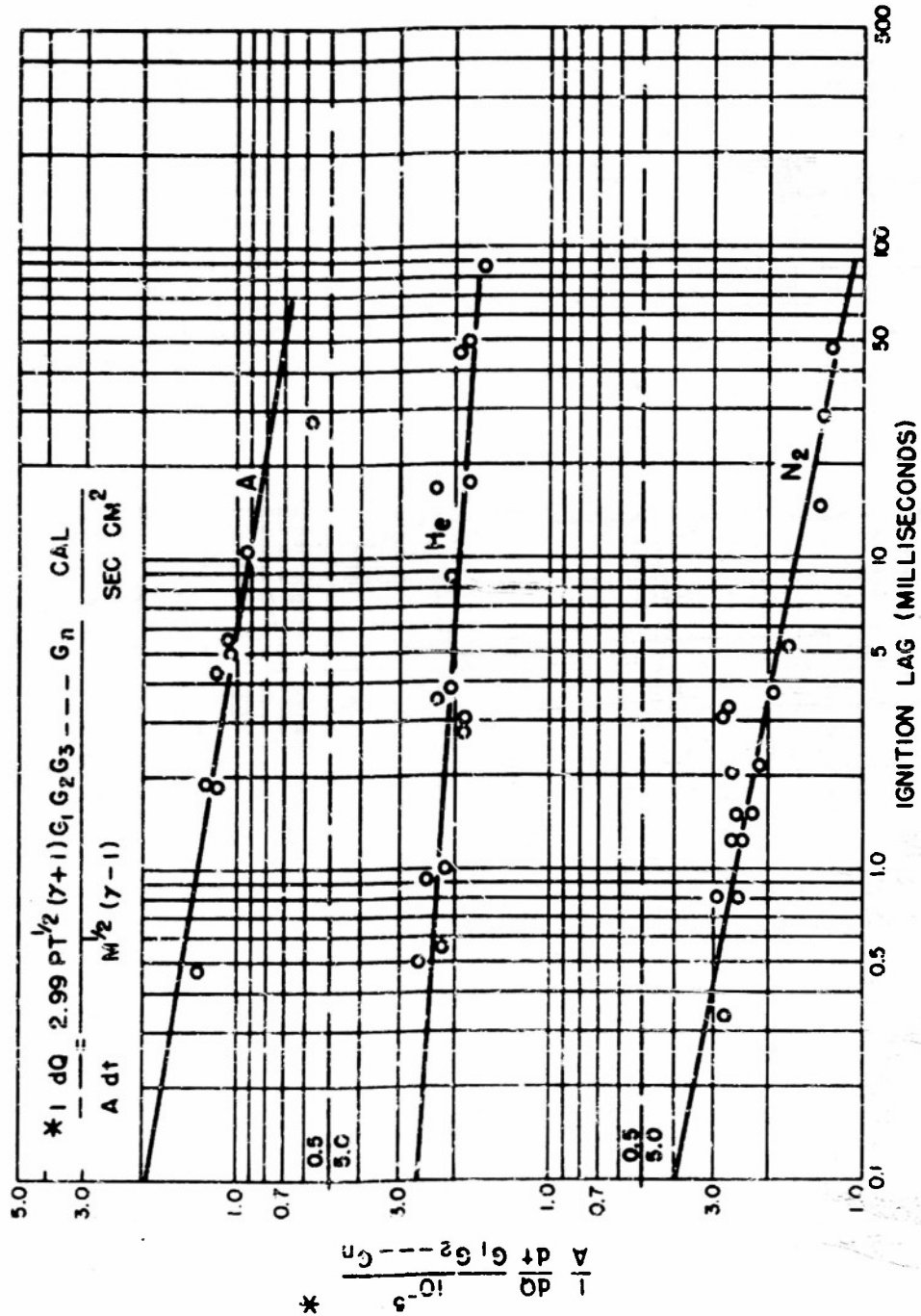


FIG. 9 FUNCTION OF HEAT FLUX VS IGNITION LAG
(NOT CORRECTED FOR SURFACE TEMPERATURE)